The Relation between Pesticidal Activities and Chemical Structures V[1]

Preparation of 1 - Alkoxynaphthalene

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Kiyoko FUJIKI

Pesticidal activities of many 1－alkoxynaphthalenes especially their 4－substituted derivatives were investigated in previous papers.[2]

The present paper deals with the preparation of 1－alkoxynaphthalene. These compounds are obtained in general by the treatment of 1－naphthol with alkyl bromide in the presence of sodium ethoxide.[3] Other method for the synthesis of 1－alkoxynaphthalene which have the lower alkyl group varying from methyl to iso－amyl except n－propyl group, involves the reaction of 1－naphthol with a mixture of lower aliphatic alcohol and concentrated sulfuric acid, previously reported by F. Yokoyama and his coworkers.[4]

In spite of the reaction which gives alkyl sulfates by the treatment of primary alcohol with sulfuric acid,[5] a modification of Yokoyama's method was used since, in my hands, it gave more satisfactory results for the preparation of 1－alkoxynaphthalene having higher alkyl group such as n－hexyl, n－octyl or n－dodecyl group.

To a homogeneous mixture of 1－naphthol and higher aliphatic alcohol was dropped concentrated sulfuric acid under stirring and warming. The resulting mixture was then refluxed for 20 hours. 1－Alkoxynaphthalene were obtained in good or moderate yield by use of fifty per cent excess of aliphatic alcohol. The results of these experiments are summerized in the Table. The structures of 1－alkoxynaphthalene were confirmed by the comparison of their infrared spectra with those of the authentic samples which were synthesized according to G. W. Gray's method,[3] and by the determination of the chemical structures of their 4－thiocyano derivatives.[6]

Experimental

The IR Spectra were recorded on a Hitachi EPI G 3 spectrophotometer.

All the chemicals were reagent grade commercial materials and used without further purification.

General Procedure.

1－Naphthol (0.1 mol) was dissolved in higher aliphatic alcohol (0.15 mol) with slight warming. To the solution was added drop by drop 4g of concentrated sulfuric acid at 50°C under stirring. The mixture was then refluxed for 20 to 23 hours, allowed to stand at room temperature, poured into 60 ml of water and the resulting oily layer

Table. Reaction of 1-Naphthol with Aliphatic Alcohol

Alkyl (m mol)		Reac. time (hr)	Yield (%)	bp°C/mmHg
n-C_3H_7	(110)	10	65.3	145/6
n-C_6H_{13}	(150)	10	78.0	164/5.5
n-C_8H_{17}	(110)	23	60.1	183/2
	(150)	10	50.2	
	(150)	20	68.0	
n-$C_{12}H_{25}$	(110)	21	40.8	204/1
	(150)	10	45.5	
	(150)	20	51.2	

was extracted with benzene. The benzene layer was washed with 10% aqueous sodium hydroxide, then with water, and dried over anhydrous sodium sulfate. The solvent and the unreacted alcohol were evaporated, and the residue was distilled *in vacuo*.

Summary

1-n-Propoxynaphthalene and other alkoxy naphthalene having higher alkyl group such as n-hexyl, n-octyl or n-dodecyl were prepared in good or moderate yield (n-C_3H_7; 65.3%, n-C_6H_{13}; 78.0%, n-C_8H_{17}; 68.0%, n-$C_{12}H_{25}$; 51.2%) by the reaction of 1-naphthol with aliphatic alcohol in the presence of concentrated sulfuric acid.

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References

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